

Transient State Work Fluctuation Theorem for a Driven Classical Dissipative System

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We derive the nonequilibrium transient state work fluctuation theorem and also the Jarzynski equality for a classical harmonic oscillator linearly coupled to a harmonic heat bath, which is dragged by an external agent. Coupling with the bath makes the dynamics not only dissipative but also non-Markovian in general. Since we do not assume anything about the spectral nature of the harmonic bath the derivation is not only restricted to the Markovian bath rather it is more general, for a non-Markovian bath.

I. INTRODUCTION

Although the field of equilibrium thermodynamics and equilibrium statistical mechanics are well explored, there existed almost no theory for systems arbitrarily far from equilibrium until the advent of fluctuation theorems (FTs)^{1,2,3,4,5,6,7} in mid 90's. In general, these fluctuation theorems have provided a general prescription on energy exchanges that take place between a system and its surroundings under general nonequilibrium conditions and explain how macroscopic irreversibility appears naturally in systems that obey time reversible microscopic dynamics. Fluctuation theorems have been cast for various nonequilibrium quantities like heat, work, entropy production etc and for systems obeying Hamiltonian⁸ as well as stochastic dynamics^{9,10}. Quantum versions of FTs are also known^{11,12}.

Apart from fluctuation theorems, Jarzynski^{13,14} had also provided a remarkable relation between the work done on a system with the equilibrium free energy difference. To illustrate the relation, consider a classical system in contact with a classical heat bath at temperature T . Initially the system was in equilibrium with the bath and then driven by some external agent (generalized force) f . Now the free energy F for the system can be calculated by computing the partition function Z_f when the generalized force is fixed at the value f , since $F_f = -\beta^{-1} \ln Z_f$, where $\beta = \frac{1}{k_B T}$, k_B is the Boltzmann constant. Let the system starts in equilibrium at time $t = 0$ specified by $f = A$ and then driven off to a later time $t = \tau$. If this process is done quasistatically then the system remains in equilibrium at each stages of the process and also at $t = \tau$ specified by $f = B$. Then the work done W on the system equals the free energy difference, $\Delta F = F_B - F_A$. On the other hand if the process is carried out with a finite rate (i.e. in nonequilibrium conditions), W will on average exceed ΔF .

$$\langle W \rangle \geq \Delta F \quad (1)$$

The external agent f is always varied in precisely the same manner from A to B . After each realization the work W performed on the system is calculated and the distribution function for W , $P(W)$ is constructed. Jarzynski derived the following mathematical

equality popularly known as the Jarzynski equality (JE) or Jarzynski relation where the angular bracket indicates the average taken over the distribution function $P(W)$.

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F) \quad (2)$$

Essentially there are two classes of fluctuation theorems, steady state^{5,7} and transient fluctuation theorems (TFT)⁶. Since the paper deals with the transient state fluctuation theorem for work here we do not discuss anything further on steady state fluctuation theorem. The transient state work fluctuation theorem gives the ratio of probabilities for the production of positive work to the production of negative work as follows,

$$\frac{P(+W)}{P(-W)} = \exp(\beta W) \quad (3)$$

Where, W is the work done on the system by an external agent for an arbitrary time period τ . The theorem holds for any value of τ , provided one starts with the system in equilibrium.

Crooks¹⁵ provided another relation for the dissipative work, W_{diss} , defined as $W_{diss} = W - \Delta F$. Where ΔF is the free energy difference between the final and the initial equilibrium state. The relation is very similar to the transient work fluctuation theorem and known as the Crooks fluctuation theorem (CFT).

$$\frac{P_F(+W_{diss})}{P_R(-W_{diss})} = \exp(\beta W_{diss}) \quad (4)$$

Here $P_R(-W_{diss})$ is the probability distribution of negative dissipative work done in a time-reversed process. Clearly $\Delta F = 0$ means $W = W_{diss}$. In such a situation the transient state fluctuation theorem for work and the Crooks fluctuation theorem are equivalent.

In this paper we derive the transient state fluctuation theorem for work for a classical harmonic oscillator coupled linearly to a harmonic bath. Because of the coupling to the bath, the system becomes dissipative. We start from a Hamiltonian description for the system plus

the harmonic heat bath and then the system is driven by an external agent for a time period of τ for a series of measurements. We analytically calculate the distribution function for work and show that it obeys the transient state fluctuation theorem. For our particular choice of the external agent the free energy change for the process is zero and hence the transient fluctuation theorem and the Crooks fluctuation theorem are same.

In recent past, experiments^{16,17} were carried out to verify the FTS. In the experiment by Wang *et al.* a colloidal particle was trapped using Laser and then dragged through a solvent and subsequently the fluctuation theorem was verified. Our Hamiltonian efficiently models such situation since the harmonic oscillator in our model could be viewed as the colloidal particle in the harmonic trap caused by Lasers and the harmonic bath as the solvent through which the colloidal particle is dragged. People have already verified FTs^{9,18,19} in the context of the above mentioned experiment. This modeling was based on a Langevin description which was Markovian. Only very recently Mai *et.al*²⁰, Speck *et.al*²¹ and Ohkuma²² *et.al* have reported derivations based on generalized Langevin equation taking care of the Non-Markovian nature of the dynamics. But here we do not start from a Langevin description rather we start with a Hamiltonian description. Since we couple our system Hamiltonian with a set of bath oscillators effectively it produces a noise acting on the system which depends on bath variable and thus the dynamics becomes stochastic. Also our derivation does not assume anything about the spectral nature of the bath and the particle coupling. Hence the results are of very general validity. The paper is arranged as follows. In the next section we define work done on the system. In section III we introduce our model. Section IV contains the detailed derivation of the fluctuation theorem and in the last section we conclude our results.

II. DEFINITION OF HEAT

According to Jarzynski¹⁴, the work done on the system (described by the Hamiltonian H_S) by an external agent f acting on the system from $t = 0$ to $t = \tau$ is defined as

$$W = \int_0^\tau \dot{f} \frac{\partial H_S}{\partial f} dt \quad (5)$$

We use this definition.

III. OUR MODEL

We consider a classical particle of mass m described by a positional coordinate x which is linearly coupled to a set of harmonic oscillators, each of unit mass described by a positional coordinate q_i ($i = 1, 2, \dots, N$) forming a

harmonic heat bath, a model for the surrounding solvent. In the experiment by Wang. *et al* the colloidal particle was dragged through the solvent by using a Laser trap. The particle experiences a harmonic trap whose minima moves in time. To model such a situation we assume that the particle x is in a harmonic well whose minima is time dependent. We thus introduce the Hamiltonian^{23,24,25}

$$H = H_S + H_B + h_{int} \quad (6)$$

where

$$H_S = \frac{p_x^2}{2m} + \frac{k}{2}(x - \alpha(t))^2$$

and

$$H_B + h_{int} = \sum_{i=1}^N \left(\frac{p_i^2}{2} + \frac{\omega_i^2}{2} \left(q_i - \frac{c_i}{\omega_i^2} x \right)^2 \right)$$

H_S is the Hamiltonian for the system, H_B is that for the harmonic bath and h_{int} represents the coupling of the system with the bath. Here p_x and p_i are the momenta for the particle and the i -th bath coordinate, k is the force constant of the optical trap and $\alpha(t)$ is the time dependent mean position of the harmonic trap.

IV. DERIVATION OF TFT FOR WORK AND JE

The time evolution of the system plus bath is governed by the Hamiltonian H . The equations of motion for the system and the bath oscillators are

$$\dot{p}_x = -\frac{\partial H}{\partial x} = -k(x - \alpha(t)) - \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} x + \sum_{i=1}^N c_i q_i \quad (7)$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} = -\omega_i^2 q_i + c_i x \quad (8)$$

$$\dot{x} = \frac{\partial H}{\partial p_x} = \frac{p_x}{m} \quad (9)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = p_i \quad (10)$$

In our case the external agent f is $\alpha(t)$ and hence the work done on the system is

$$W = \int_0^\tau \dot{\alpha}(t) \frac{\partial H_S}{\partial \alpha} dt = \int_0^\tau -k\dot{\alpha}(t)(x(t) - \alpha(t)) dt. \quad (11)$$

Thus within the harmonic Hamiltonian description the work done on the system W is linear in x . As our Hamiltonian is quadratic and we shall assume equilibrium distributions for the initial distribution for the initial conditions, W would have a Gaussian probability distribution²⁰ with a mean $\langle W \rangle$ and the variance $\sigma_W^2 = \langle W^2 \rangle - \langle W \rangle^2$. So the distribution function for W is

$$P(W) = \frac{1}{\sqrt{2\pi\sigma_W^2}} e^{-(W-\langle W \rangle)^2/2\sigma_W^2} \quad (12)$$

with

$$\langle W \rangle = \int_0^\tau -k\dot{\alpha}(t)(\langle x(t) \rangle - \alpha(t))dt \quad (13)$$

and

$$\sigma_W^2 = k^2 \int_0^\tau dt_1 \int_0^\tau dt_2 \dot{\alpha}(t_1) \dot{\alpha}(t_2) C(t_1, t_2) \quad (14)$$

with $\Delta x(t_1) = x(t_1) - \langle x(t_1) \rangle$ and $C(t_1, t_2) = \langle \Delta x(t_1) \Delta x(t_2) \rangle$.

With the above Gaussian distribution function for work it is easy to show that $\frac{P(W)}{P(-W)} = e^{\frac{2W\langle W \rangle}{\sigma_W^2}}$. So in order to satisfy the TFT for work it is enough to show that $\sigma_W^2 = \frac{2\langle W \rangle}{\beta}$.

Now it is obvious that to calculate the work done, its mean and the variance one has to know x as a function of time t . To find x as a function of time t we proceed as follows. We take a Laplace transform of Eq. (7) and Eq. (8) to get.

$$\tilde{x}(s) = \frac{\left(k\tilde{\alpha}(s) + m\dot{x}(0) + \sum_{i=1}^N c_i \tilde{q}_i(s) + msx(0) \right)}{\left(ms^2 + k + \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} \right)} \quad (15)$$

and

$$\tilde{q}_i(s) = \frac{(p_i(0) + sq_i(0) + c_i \tilde{x}(s))}{(s^2 + \omega_i^2)} \quad (16)$$

Now we substitute $\tilde{q}_i(s)$ in Eq. (15) from Eq. (16) and get $\tilde{x}(s)$ in terms of the initial momenta and position of the bath coordinates in time and that of the system itself.

$$\tilde{x}(s) = k\tilde{\alpha}(s) + (p_x(0) + mx(0)s + \tilde{g}(s))\tilde{b}(s) \quad (17)$$

Where

$$\tilde{b}(s) = \frac{1}{\left(k + ms^2 + \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} - \sum_{i=1}^N \frac{c_i^2}{(s^2 + \omega_i^2)} \right)} \quad (18)$$

and

$$\tilde{g}(s) = \sum_{i=1}^N c_i \frac{(p_i(0) + sq_i(0))}{(s^2 + \omega_i^2)} \quad (19)$$

Taking the inverse Laplace transform of Eq. (17) one gets $x(t)$.

$$x(t) = mx(0)y(t) + mv(0)b(t) + \int_0^t dt' b(t-t') (k\alpha(t') + \xi(t')) \quad (20)$$

with

$$\xi(t) = g(t) - \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} \cos(\omega_i t) x(0)$$

and

$$y(t) = \int_0^t dt' \left(\dot{b}(t') \delta(t-t') + \frac{1}{m} \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} \cos(\omega_i t') b(t-t') \right)$$

Now Eq. (20) should be consistent with the initial

conditions. This readily gives

$$my(0) = 1 \quad (21)$$

$$mb(0) = 0 \quad (22)$$

$$m\dot{b}(0) = 1 \quad (23)$$

$$m\dot{y}(0) = 0 \quad (24)$$

One can substitute $x(t)$ from Eq. (20) to Eq. (11) to calculate W . Next task is to calculate $\langle W \rangle$ which is

obtained from Eq. (11) by replacing $x(t)$ with its thermal average

$$\langle x(t) \rangle = m \langle x(0) \rangle y(t) + m \langle v(0) \rangle b(t) + \int_0^t dt' b(t-t') (k\alpha(t') + \langle \xi(t') \rangle) \quad (25)$$

Here the angular bracket indicates a thermal average taken in the initial state of the harmonic bath (at $t = 0$) with the shifted canonical equilibrium distribution (since we start from an initial equilibrium distribution) given

by $\rho \sim e^{-\beta H^{(0)}}$. Thus $\langle p_x(0) \rangle = 0$, $\langle x(0) \rangle = \alpha(0)$. Now to calculate $\langle g(t) \rangle$ we proceed as follows. First we take the inverse Laplace transform of Eq. (19) to get

$$g(t) = \sum_{i=1}^N c_i \left\{ p_i(0) \frac{\sin(\omega_i t)}{\omega_i} + q_i(0) \cos(\omega_i t) \right\} \quad (26)$$

Next we take the thermal average with respect to the initial distribution $\rho \sim e^{-\beta H^{(0)}}$ to get

$$\langle g(t) \rangle = \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} x(0) \cos(\omega_i t) \quad (27)$$

as $\langle p_i(0) \rangle = 0$, $\langle q_i(0) \rangle = \frac{c_i}{\omega_i^2} x(0)$. Thus $\langle \xi(t) \rangle = \langle g(t) \rangle - \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} \cos(\omega_i t) x(0) = 0$. The quantity $\xi(t)$ is a Gaussian random force from the bath with the statistical properties, $\langle \xi(t) \rangle = 0$, $\langle \xi(t) \xi(t') \rangle = \beta^{-1} \Gamma(t - t')$, where $\Gamma(t) = \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} \cos(\omega_i t)$.

Finally we get

$$\langle x(t) \rangle = m\alpha(0)y(t) + \int_0^t dt' k\alpha(t')b(t-t') \quad (28)$$

Next we derive a set of equations in the Laplace and the time domain. These are used to get the TFT for work.

In a few steps one can show, $ms\tilde{y}(s) = 1 - k\tilde{b}(s)$, where $y(s) = s\tilde{b}(s) + \frac{\tilde{\Gamma}(s)}{m}\tilde{b}(s)$, $\tilde{\Gamma}(s) = \sum_{i=1}^N \frac{sc_i^2}{\omega_i^2(s^2 + \omega_i^2)}$. Inverse Laplace transform of $ms\tilde{y}(s) = 1 - k\tilde{b}(s)$ gives $\dot{y}(t) = -(\frac{k}{m})b(t)$. Also $s\tilde{b}(s) = \tilde{y}(s) - \frac{\tilde{\Gamma}(s)}{m}\tilde{b}(s)$ whose inverse Laplace gives $\dot{b}(t) = y(t) - \frac{1}{m} \int_0^t dt' \Gamma(t')b(t-t')$. So we have the following set of important relations in the Laplace and the time domain.

$$ms\tilde{y}(s) = 1 - k\tilde{b}(s)$$

$$s\tilde{b}(s) = \tilde{y}(s) - \frac{1}{m}\tilde{\Gamma}(s)\tilde{b}(s)$$

$$\dot{y}(t) = -\left(\frac{k}{m}\right)b(t) \quad (29)$$

$$\dot{b}(t) = y(t) - \frac{1}{m} \int_0^t dt' \Gamma(t')b(t-t')$$

Using the above set of equations one can show that the average work done on the system (which is given by Eq. (13)) is

$$\langle W \rangle = \left(\frac{m}{k}\right) \int_0^\tau dt \int_0^t dt' k\dot{\alpha}(t)y(t-t')k\dot{\alpha}(t') \quad (30)$$

To derive it we proceed as follows. First we replace $\langle x(t) \rangle$ in Eq. (13) from Eq.(28) to get

$$\langle W \rangle = \frac{k}{2} \left(\frac{\alpha^2(\tau)}{2} - \frac{\alpha^2(0)}{2} \right)$$

$$- \int_0^\tau dt k m \alpha(0) \dot{\alpha}(t) y(t) - \int_0^\tau dt \int_0^t dt' k \dot{\alpha}(t) b(t-t') k \dot{\alpha}(t')$$

and then using Eq. (29) followed by an integration by parts and using Eq. (21) one ultimately gets

$$\langle W \rangle = \left(\frac{m}{k}\right) \int_0^\tau dt \int_0^t dt' k\dot{\alpha}(t)y(t-t')k\dot{\alpha}(t')$$

which is Eq. (30).

In order to evaluate the variance we first have to calcu-

late the correlation function, $C(t_1, t_2) = \langle \Delta x(t_1) \Delta x(t_2) \rangle$. Now using Eq. (20) one can show

$$C(t_1, t_2) = m^2 (k\beta)^{-1} y(t_1)y(t_2) + m^2 (m\beta)^{-1} b(t_1)b(t_2) + \beta^{-1} \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 b(t_1 - t'_1)b(t_2 - t'_2)\Gamma(t'_1 - t'_2) \quad (31)$$

Where we have used $\langle \xi(t)\xi(t') \rangle = \beta^{-1}\Gamma(t - t')$, $\langle (x(0) - \alpha(0))^2 \rangle = (k\beta)^{-1}$, $\langle v^2(0) \rangle = (m\beta)^{-1}$.

The above expression for $C(t_1, t_2)$ is then put back in Eq. (14) to get

$$\sigma_W^2 = \left(\frac{m^2}{\beta k}\right) \left(\int_0^\tau dt k\dot{\alpha}(t)y(t)\right)^2 + \left(\frac{m}{\beta}\right) \left(\int_0^\tau dt k\dot{\alpha}(t)b(t)\right)^2 + \frac{1}{\beta} \int_0^\tau dt_1 \int_0^\tau dt_2 \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 \Gamma(t'_1 - t'_2) k\dot{\alpha}(t_1)b(t_1 - t'_1)b(t_2 - t'_2)k\dot{\alpha}(t_2) \quad (32)$$

Let us define

$$J(t_1, t_2) = \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 \Gamma(t'_1 - t'_2) b(t_1 - t'_1)b(t_2 - t'_2)$$

With the help of Laplace and Fourier transform one can show (see Appendix for the evaluation of the integral)

$$J(t_1, t_2) = \left(\frac{m}{k}\right) y(t_1 - t_2) - \left(\frac{m^2}{k}\right) y(t_1)y(t_2) - mb(t_1)b(t_2) \quad (33)$$

When the above expression for $J(t_1, t_2)$ is plugged into Eq. (32) one gets

$$\sigma_W^2 = \left(\frac{m}{k\beta}\right) \int_0^\tau dt_1 \int_0^\tau dt_2 k\dot{\alpha}(t_1)y(t_1 - t_2)k\dot{\alpha}(t_2)$$

In Eq. (30). t and t' being dummy variables one can change these into t_1 and t_2 respectively and rewrite Eq. (30).

$$\langle W \rangle = \left(\frac{m}{k}\right) \int_0^\tau dt_1 \int_0^{t_1} dt_2 k\dot{\alpha}(t_1)y(t_1 - t_2)k\dot{\alpha}(t_2) \quad (34)$$

Now we interchange t_1 and t_2 .

$$\langle W \rangle = \left(\frac{m}{k}\right) \int_0^\tau dt_2 \int_0^{t_2} dt_1 k\dot{\alpha}(t_2)y(t_2 - t_1)k\dot{\alpha}(t_1) \quad (35)$$

Adding Eq. (34). and Eq. (35). Since $y(t)$ is an even function of t and also $\tau > t_1, \tau > t_2$ one gets

$$2\langle W \rangle = \left(\frac{m}{k}\right) \int_0^\tau dt_1 \int_0^\tau dt_2 k\dot{\alpha}(t_1)y(t_1 - t_2)k\dot{\alpha}(t_2) = \beta\sigma_W^2$$

This shows that the TFT for work is satisfied. Next we come to Crooks fluctuation theorem. As we have mentioned earlier that TFT for work and CFT becomes equivalent when the free energy change for the concerned process becomes zero ($\Delta F = 0$, $W = W_{diss}$) which happens in our case. This is because we assumed the external agent is the time dependent mean position of the harmonic trap and subsequently when one evaluates the partition function by performing a Gaussian integral, $\alpha(t)$ does not appear in the partition function and thus the free energy becomes independent of $\alpha(t)$ so the free energy change is zero. Hence the TFT for work reads as

$$\frac{P(+W)}{P(-W)} = \exp(\beta W) \quad (36)$$

JE is obtained easily by integrating above equation

$$\begin{aligned} \langle \exp(-\beta W) \rangle &= \int_{-\infty}^{\infty} dW P(+W) \exp(-\beta W) \\ &= \int_{-\infty}^{\infty} dW P(-W) = 1 \end{aligned}$$

V. CONCLUSIONS

The paper verifies the TFT for work and the JE for a classical dissipative system which is dragged through by an external agent. We start from a Hamiltonian description of our system which is linearly coupled to a bath. The coupling makes the dynamics stochastic and non-Markovian in general. A non-Markovian bath is more realistic because of the existence of finite correlation time of the noise acting on the particle. As far as our knowledge goes this is the first detailed derivation of the TFT for work for such classical dissipative system starting from a Hamiltonian description rather than from a Langevin equation. To keep our derivation analytic we had to restrict ourselves to a harmonic system and a harmonic bath.

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VII. APPENDIX

The integral $J(t_1, t_2)$ is evaluated as follows. First let us consider the integral

$$\int_0^\infty dt_2 e^{-s_2 t_2} \int_0^{t_2} dt'_2 b(t_2 - t'_2) e^{-i\omega t'_2} = b(s_2) \int_0^\infty dt_2 e^{-s_2 t_2} e^{-i\omega t_2} = b(s_2) \frac{e^{-(s_2 + i\omega)t_2}}{(s_2 + i\omega)} \Big|_0^\infty = \frac{b(s_2)}{(s_2 + i\omega)} \quad (37)$$

Similarly

$$\int_0^\infty dt_1 e^{-s_1 t_1} \int_0^{t_1} dt'_1 b(t_1 - t'_1) e^{i\omega t'_1} = \frac{b(s_1)}{(s_1 - i\omega)} \quad (38)$$

Then with the help of Eq. (37) and Eq. (38) double Laplace transform of $J(t_1, t_2)$ can be written as

$$\tilde{J}(s_1, s_2) = \int_0^\infty dt_1 e^{-s_1 t_1} \int_0^\infty dt_2 e^{-s_2 t_2} \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 \Gamma(t'_1 - t'_2) b(t_1 - t'_1) b(t_2 - t'_2) \quad (39)$$

We also define

$$\Gamma(t'_1 - t'_2) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty d\omega \tilde{\Gamma}(\omega) e^{i\omega(t'_1 - t'_2)} \text{ and}$$

$$\tilde{\Gamma}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty dt \Gamma(t) e^{-i\omega t}$$

Then after some algebraic manipulations Eq. (39) becomes

$$\begin{aligned} \tilde{J}(s_1, s_2) &= \int_0^\infty dt_1 e^{-s_1 t_1} \int_0^\infty dt_2 e^{-s_2 t_2} \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 b(t_1 - t'_1) b(t_2 - t'_2) \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty d\omega \tilde{\Gamma}(\omega) e^{i\omega(t'_1 - t'_2)} \right) \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty d\omega \frac{\tilde{b}(s_1) \tilde{b}(s_2) \tilde{\Gamma}(\omega)}{(s_1 - i\omega)(s_2 + i\omega)} = \frac{\tilde{b}(s_1) \tilde{b}(s_2)}{(s_1 + s_2) \sqrt{2\pi}} \int_{-\infty}^\infty d\omega \left(\frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} + \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} \right) \end{aligned} \quad (40)$$

Next consider the integral $\frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty d\omega \frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega}$ which can be evaluated as follows

$$\tilde{J}(s_1, s_2) = \frac{\tilde{b}(s_1) \tilde{b}(s_2)}{(s_1 + s_2) \sqrt{2\pi}} \int_{-\infty}^\infty d\omega \left(\frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} + \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} \right) \quad (41)$$

$$\begin{aligned} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{d\omega}{(s_1 - i\omega)} \int_{-\infty}^{\infty} dt e^{-i\omega t} \Gamma(t) = \int_{-\infty}^{\infty} dt \Gamma(t) \left(\frac{1}{-2\pi i} \int_{-\infty}^{\infty} \frac{d\omega}{(\omega + is_1)} e^{-i\omega t} \right) = \\ &= \int_{-\infty}^{\infty} dt \Gamma(t) \Theta(t) e^{-s_1 t} = \int_0^{\infty} dt \Gamma(t) e^{-s_1 t} = \tilde{\Gamma}(s_1) \end{aligned} \quad (42)$$

Similarly

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} = \tilde{\Gamma}(s_2) \quad (43)$$

$$\tilde{J}(s_1, s_2) = \left(\frac{m}{k}\right) y(t_1 - t_2) - \left(\frac{m^2}{k}\right) y(t_1) y(t_2) - m b(t_1) b(t_2) \quad (45)$$

Now we use Eq. (42) and Eq. (43) to get

$$\tilde{J}(s_1, s_2) = \frac{\tilde{b}(s_1) + \tilde{b}(s_2)}{(s_1 + s_2)} \left(\tilde{\Gamma}(s_1) + \tilde{\Gamma}(s_2) \right) \quad (44)$$

$$J(t_1, t_2) = \left(\frac{m}{k}\right) y(t_1 - t_2) - \left(\frac{m^2}{k}\right) y(t_1) y(t_2) - m b(t_1) b(t_2)$$

The above Eq. is then simplified with the help of the Eq. (29) to get

which is Eq. (33).

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- ¹ J. Kurchan, J. Stat. Mech. Theory Exp. **P07005** (2007).
² E. Sevick, R. Prabhakar, and S. R. Williams, arXiv:0709.3888 [cond-mat.stat-mech] (2007).
³ F. Ritort, arXiv:0705.0455 [cond-mat.stat-mech] (2007).
⁴ C. Bustamante, J. Liphardt, and F. Ritort, Phys. Today **58**, 43 (2005).
⁵ D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
⁶ D. J. Evans and D. J. Searles, Phys. Rev. E **50**, 1645 (1994).
⁷ G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2684 (1995).
⁸ E. Schöll-Paschinger and C. Dellago, J. Chem. Phys. **125**, 054105 (2006).
⁹ R. van Zon and E. G. D. Cohen, Phys. Rev. E **67**, 046102 (2003).
¹⁰ J. Kurchan, J. Phys. A: Math. Gen. **31**, 3719 (1998).
¹¹ D. K. Wojcik and C. Jarzynski, Phys. Rev. Lett. **92**, 230602 (2004).
¹² M. Esposito and S. Mukamel, Phys. Rev. E **73**, 046129 (2006).
¹³ C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
¹⁴ C. Jarzynski, J. Stat. Mech. Theory Exp. **P9005** (2004).
¹⁵ G. Crooks, Phys. Rev. E **60**, 2721 (1999).
¹⁶ G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002).
¹⁷ G. M. Wang, J. C. Reid, D. M. Carberry, D. R. M. Williams, E. M. Sevick, and D. J. Evans, Phys. Rev. E **71**, 046142 (2005).
¹⁸ R. D. Astumian, J. Chem. Phys. **126**, 111102 (2007).
¹⁹ A. Saha and J. K. Bhattacharjee, J. Phys. A: Math. Theor. **40**, 13269 (2007).
²⁰ T. Mai and A. Dhar, Phys. Rev. E **75**, 061101 (2007).
²¹ T. Speck and U. Seifert, J. Stat. Mech. Theory Exp. **L09002** (2007).
²² T. Ohkuma and T. Ohta, J. Stat. Mech. Theory Exp. **P10010** (2007).
²³ R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).
²⁴ U. Weiss, *Quantum Dissipative Systems* (World Scientific, 1999).
²⁵ R. Zwanzig, J. Stat. Phys. **9**, 215 (1973).